Electron paramagnetic resonance in a scanning tunneling microscope

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A scanning tunneling microscope can be used to observe ESR with a spatial resolution at the atomic scale.

The scanning tunneling microscope has been used as a spectroscopic instrument to measure the local density of states with a spatial resolution at the atomic scale and even to detect individual spins at paramagnetic centers near a surface. Demuth's group[1] measured the frequency spectrum of the tunneling current in a static magnetic field. When the tip was positioned above a paramagnetic center at the Si(111) surface, a sharp peak was observed in the frequency spectrum, at a frequency corresponding to the precession frequency of the localized spin. This method makes it possible to detect the positions of paramagnetic centers with an atomic-scale resolution. McKinnon *et al.*[2] recently demonstrated a different formulation of the experiment: In addition to the static magnetic field, they used a weak field directed perpendicular to the static field and rotating at a frequency ω (this field configuration corresponds to ESR experiments). They measured the time evolution of the tunneling current with the help of a lock-in detector.[2] The test sample was an organic molecule with free radicals, which served as centers with localized spins. When the frequency of the rotating field corresponded to the ESR frequency of a localized spin, and the tip was positioned above the center, oscillations at the field frequency were seen in the tunneling current. As the tip was withdrawn from the center (with no change in frequency), the signal disappeared. The reason for the current modulation is not totally clear; in this letter we propose one possible explanation.

The fact that the signal disappears as the needle is moved away from the center indicates that the ESR frequencies of the delocalized electrons and of the spin at the center are different. This point is of assistance in constructing a theory, although it is not of fundamental importance. We make the further assumption that the field frequency ω is close to the ESR frequency of the spin at the center.

The problem is basically one of calculating the tunneling current as a function of the time. To describe the tunneling between the crystal and the tip, we use the method of a tunneling Hamiltonian. In the basis of localized orbitals, this Hamiltonian is

$$\hat{H}_t = \sum_{\substack{j,n,\sigma \\ j',n'}} [T^{jn\sigma}_{j'n'\sigma} c^{+}_{cjn\sigma} c_{tj'n'\sigma} + \text{H.a.}], \tag{1}$$

where the subscripts c and t specify the crystal and the tip, and $T^{jn\sigma}_{j'n'\sigma}$ describes hops of electrons from the $|\varphi_{n\sigma}(\vec{r}-\vec{R}_j)\rangle$ orbital in the crystal to $|\varphi_{n'\sigma}(\vec{r}-\vec{R}_{j'})\rangle$ orbitals in the tip. We assume that the interaction of the localized spin $\vec{S}$ with the delocalized

electrons is described by the exchange interaction

$$\hat{H}_{ex} = \sum_{\sigma,\sigma'} [J_{j_0 n_0}(\vec{\sigma}_{\sigma\sigma'}\vec{S}(t)) c^{+}_{cj_0 n_0 \sigma} c_{cj_0 n_0 \sigma'} + \text{H.a.}], \tag{2}$$

where $J_{j_0 n_0}$ is the constant of the exchange interaction of electrons with a spin at the center $\vec{R}_{j_0}$. When there is a time-varying external magnetic field, the behavior of a localized spin can be determined from the Bloch equations

$$\frac{dS_{\pm}(t)}{dt} \pm i\omega_L S_{\pm} + \frac{S_{\pm}}{\tau_2} = \pm i S_z h_1 e^{\pm i\omega t},$$

$$\frac{dS_z(t)}{dt} - \frac{S_z}{\tau_2} = \frac{1}{2} ig[S_+ e^{-i\omega t} - S_- e^{i\omega t}]h_1 + \frac{S_{z0}}{\tau_1}, \tag{3}$$

where $\omega_L = gH_z$ is the Larmor frequency, g is the g-factor, τ_1 and τ_2 are the longitudinal and transverse relaxation times, S_{z0} is the equilibrium magnetization in the static field H_z, h_1 is the perpendicular component of the rotating field ($h_1 \ll H_z$), and ω is the field frequency.

The time-dependent tunneling current can be written in terms of Keldysh Green's functions:[3,4]

$$I(t) = \frac{e}{h} \text{Tr}\{\int dt'[\hat{T}\hat{g}^{+}_t(t,t')\hat{T}^{+}\hat{G}^{-}_c(t',t) - \hat{T}^{+}\hat{G}^{+}_c(t,t')\hat{T}\hat{g}^{-}_t(t',t)]\}, \tag{4}$$

where the Tr (trace) is over the orbital, site, and spin indices. The calculation of the Green's function of the crystal, $\hat{G}^{\pm}_c(t',t)$, must incorporate the interaction with the localized spin. We assume that the spin–orbit coupling in the crystal is negligible. Then components $\hat{G}^{\pm}_c(t',t)$, which are not diagonal in the spin arise because of the field $\vec{h}_1(t)$ and the interaction with the spin $\vec{S}(t)$ (as a result of spin–flip processes). Under the assumption that the field frequency coresponds to the ESR of the localized spin, and under the further assumption that there is a frequency difference between the resonances of a spin at a center and those of the spins of delocalized electrons (because of, for example, different g-factors), the off-diagonal components of $\hat{G}^{\pm}_c$ are more important, because of the interaction with the localized spin. In this case we have

$$\hat{G}^{\pm\uparrow\downarrow}_c(t,t') \tag{5}$$

$$= \int dt_1[\hat{g}^{R\uparrow\uparrow}_c(t,t'_1)\hat{J}S_+(t_1)\hat{g}^{\pm\downarrow\downarrow}_c(t_1,t') + \hat{g}^{\pm\uparrow\uparrow}_c(t,t'_1)\hat{J}S_+(t_1)\hat{g}^{A\downarrow\downarrow}_c(t_1,t')].$$

The Green's functions of the tip and the crystal (which do not interact with each other) can be written as follows in the basis of localized orbitals:

$$\hat{g}^{\pm}_{c,t} = \{g^{\pm jn\sigma}_{c,tj'n'\sigma'}\} = \langle \varphi_{n\sigma}(\vec{r} - \vec{R}_j)|\hat{g}^{\pm}_{c,t}(\epsilon)|\varphi_{n'\sigma'}(\vec{r} - \vec{R}_{j'})\rangle$$

$$= 2\pi i \rho^{jn\sigma}_{c,tj'n'\sigma'} \begin{cases} f_{c,t}(\epsilon) \\ f_{c,t}(\epsilon) - 1, \end{cases} \tag{6}$$

$$\rho^{jn\sigma}_{j'n'\sigma'}(\epsilon) = \sum_{\mu} A^{jn\sigma}_{\mu} \delta(\epsilon - \epsilon_{\mu}) A^{*j'n'\sigma'}_{\mu},$$

where A is the matrix of the expansion of the crystal or tip eigenvectors in localized orbitals, the matrix $\hat{\rho}$ is the density of states, and

$$|\Psi_{\mu}> = \sum_{j,n,\sigma} A^{jn\sigma}_{\mu} |\varphi_{n\sigma}(\vec{r} - \vec{R}_j)> . \tag{7}$$

We furthermore assume that the electrons in the tip are not at resonance. It follows from (4) that, because of the trace, the Green's function of the tip must have components which are not diagonal in spin projections. In the actual experiments, heavy metals (W, Pt, Ir, Au, and alloys thereof) are used as the tip material. The spin–orbit coupling in such cases is strong ($\lambda_{so} = 1$ eV). The components which are not diagonal in the spin are thus more important—because of the spin–orbit coupling—than the corrections for $\vec{h}_1(t)$. We assume that the spin–orbit coupling has already been incorporated in (6).

The oscillatory increment in the tunneling current can be written in the form (we are writing out the spin indices explicitly)

$$\begin{aligned}\delta I(t) = \frac{2\pi e}{\hbar} \mathrm{Sp}\{ \int d\epsilon [& S^0_+ e^{i\omega t} (\hat{T} \hat{\rho}_t^{\downarrow\uparrow}(\epsilon) \hat{T}^+ \hat{\rho}_c^{\uparrow\uparrow}(\epsilon + \omega) \hat{J} \hat{\rho}_c^{\downarrow\downarrow}(\epsilon) \\ & + \hat{T} \hat{\rho}_t^{\downarrow\uparrow}(\epsilon) \hat{T}^+ \hat{\rho}_c^{\uparrow\uparrow}(\epsilon) \hat{J} \hat{\rho}_c^{\downarrow\downarrow}(\epsilon - \omega)) f_t(\epsilon)[1 - f_c(\epsilon)] \\ & - S^0_+ e^{i\omega t} (\hat{T}^+ \hat{\rho}_c^{\uparrow\uparrow}(\epsilon + \omega) \hat{J} \hat{\rho}_c^{\downarrow\downarrow}(\epsilon) \hat{T} \hat{\rho}_t^{\downarrow\uparrow}(\epsilon) \\ & + \hat{T}^+ \hat{\rho}_c^{\uparrow\uparrow}(\epsilon) \hat{J} \hat{\rho}_c^{\downarrow\downarrow}(\epsilon - \omega) \hat{T} \hat{\rho}_t^{\downarrow\uparrow}(\epsilon)) f_c(\epsilon)[1 - f_t(\epsilon)]] \\ & + (\uparrow \rightleftharpoons \downarrow, S^+ \to S^-, \omega \to -\omega)\}.\end{aligned} \tag{8}$$

The indicated replacements are to be made in the second part of this formula. The applied voltage is incorporated in $f_{c,t}(\epsilon)$. Under the assumption $\omega \simeq \omega_L$, and under the further assumption that ω is lower than the characteristic energies over which $\rho_{c,t}(\epsilon)$ vary, we find

$$I(t) = \frac{8\pi e}{\hbar} \mathrm{Re}\{S^0_+ e^{i\omega t}\} \mathrm{Tr}\{ \int d\epsilon [\hat{T} \hat{\rho}_t^{\sigma - \sigma}(\epsilon) T^+ \hat{\rho}_c^{-\sigma - \sigma}(\epsilon) \hat{J} \hat{\rho}_c^{\sigma\sigma}(\epsilon)][f_t - f_c]. \tag{9}$$

The amplitude S^0_+ should be found from Bloch equations (3). As a rule, the passage through resonance is adiabatically slow (the passage can be arranged by, for example, varying the field H_z at a fixed position of the tip). In this case we have[5]

$$\begin{aligned} S^0_{\pm} &= g h_1 S_z \frac{e^{\pm i\omega t}}{\omega - \omega_L \mp i/\tau_2}, \\ S_z &= S_{0z} \frac{1 + (\omega - \omega_L)^2 \tau_2^2}{1 + (\omega - \omega_L)^2 \tau_2^2 + g^2 h_1^2 \tau_1 \tau_2}. \end{aligned} \tag{10}$$

Exactly at the resonance, at $\omega = \omega_L$, we find

$$\delta I(t) = \frac{16\pi e}{\hbar} V |T^{jn}_{j_0 n_0}|^2 \rho^{in\uparrow\downarrow}_{tjn}(\epsilon_F)(\rho^{j_0 n_0}_{j_0 n_0}(\epsilon_F))^2 \frac{Jgh_1\tau_2 \sin(\omega_L t)}{1+(\omega-\omega_L)^2\tau_2^2 + g^2 h_1^2 \tau_1 \tau_2}. \quad (11)$$

In deriving (11) we assumed that $f_{c,t}$ are Fermi functions. Here ϵ_F is the Fermi energy in the tip; $\rho^{j_0 n_0}_{j_0 n_0}(\epsilon_F)$ is the local density of delocalized electrons at the paramagnetic center (we are ignoring the corrections for H_z); $\rho_c^{\uparrow\uparrow} = \rho_c^{\downarrow\downarrow} = \rho_c$, $\rho^{jn\uparrow\downarrow}_{tjn}(\epsilon_F)$ is the partial density of states at that atom of the tip which is closest to the paramagnetic center; $|T^{jn}_{j_0 n_0}| \propto e^{-a|\vec{R}_{j_0} - \vec{R}_j|}$ is the overlap integral of the orbitals at the center of the tip and at the outermost atom of the tip; and V is the applied voltage. As the tip is moved away from the center, $\delta I(t)$ falls off exponentially with the distance.

A solution of (3) for $S^{\pm}(t)$, for an adiabatically slow passage through the resonance, exists if the condition $1/\tau_1 h_1 \ll 1$ holds.[5] Consequently, in a static magnetic field the relative size of the oscillatory increment $\delta I(t)$ against the background of the steady-state component of the tunneling current, I_0, is $\delta I(t)/I_0 \propto \sin(\omega_L t)(J/w)/\tau_1 h_1$ in order of magnitude and small in proportion to the parameter $\tau_1 h_1$ (here w is on the order of the width of the delocalized-electron band: $w \propto 1/\rho_c$). In the case of a fast passage through resonance ($1/\tau_1 \ll |dH_z/dt|/H_z \ll g h_1$—a rapid variation of the field H_z), it follows from (3) that we should take $S^{\pm}(t)$ to be[5]

$$S^{\pm} \propto \frac{g h_1 S_{0z}}{\omega - \omega_L} e^{\mp i\omega t}, \quad (12)$$

and there is a sharp resonance.

In the case in which there is a magnetizing field which remains constant over time (this is the case experimentally), and there is also a field $\vec{h}_1(t)$ which is rotating at a fixed frequency, the relative quantity $\delta I(t)/I_0$ is always limited to a value $1/\tau_1 h_1 \ll 1$. If the ESR frequencies for the localized spin and the delocalized electrons are the same (i.e., if they differ by an amount smaller than the width of the resonance for the spin at the center), then the oscillations in the current persist, but the spatial sensitivity disappears (the oscillations do not die out when the tip is moved away from the oscillation center).

At a qualitative level, the reason for the oscillations in the current can be explained as follows. We ignore the magnetization of the delocalized electrons in the crystal and in the tip by the fields H_z and h_1. We consider the effect of the field on the localized spin alone. As it is scattered by the center, the electron acquires a spin component perpendicular to H_z because of the effective field of the spin, with an amplitude $\propto h_1/(\omega - \omega_L)$. The density matrix becomes nondiagonal in the spin: $\rho_c^{\uparrow\downarrow} \propto \rho_c^{\uparrow}\rho_c^{\downarrow} h_1/(\omega - \omega_L)$. The probability that an electron with a perpendicular spin component will tunnel into the tip is nonzero if the density matrix in the tip also has components which are not diagonal in the spin (such components arise because of the spin–orbit coupling). The extent to which the spin turns is modulated at the frequency ω because of the field h_1. It is this modulation which leads to the modulation of the current.

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